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- (71) Applicant (for all designated States except US): MAXWELL TECHNOLOGIES, INC. [US/US]; 9244 Balboa Avenue, San Diego, California 92123 (US).
- (72) Inventors; and
- Inventors/Applicants (for US only): ZHONG, Linda [US/US]; 5849 Aster Meadows Place, San Diego, California 92130 (US). XI, Xiaomei [US/US]; 3537 Cay Drive, Carlsbad, California 92130 (US). MITCHELL, Porter [US/US]; 7155 Torrey Mesa Court, San Diego, California 92129 (US).
- (74) Agent: OSBORNE, Thomas J. Jr.; Hensley Kim & Holzer, LLC, 1660 Lincoln Street, Suite 3000, Denver, Colorado 80264 (US).

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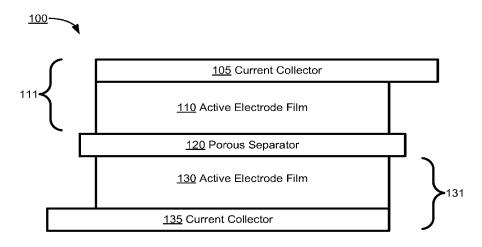


Fig. 1

(57) Abstract: An electrode with a current collector having between about substantially no magnesium and less than about 0.7% magnesium by weight. The current collector may be connected to electrode material to obtain an electrode for use in various electrical devices, including a double layer capacitor. The reduced magnesium aluminum of the current collector and/or packaging decreases current leakage of the capacitor.



ULTRACAPACITOR COLLECTOR AND/OR PACKAGE WITH CONTROLLED MAGNESIUM CONTENT

BACKGROUND

[0001] This application claims the benefit of United States nonprovisional application no. 11/679,783 filed 27 February 2007, which is hereby incorporated by reference as though fully set forth herein.

[0002] The present invention generally relates to energy storage devices and the fabrication of energy storage devices. More specifically, the present invention typically relates to ultracapacitors or electrochemical double layer capacitors which may be used in/as energy storage devices.

[0003] Electrical energy storage cells are widely used to provide power to electronic, electrical, electromechanical, electrochemical, and other useful devices. Such cells include primary (non-rechargeable) battery cells, secondary (rechargeable) battery cells, fuel cells, and capacitors. Important characteristics of electrical energy storage devices include energy density, power density, maximum charging rate, internal leakage current, equivalent series resistance (ESR), and/or durability, i.e., the ability to withstand multiple charge-discharge cycles. For a number of reasons, double layer capacitors, also known as supercapacitors and ultracapacitors, are gaining popularity in many energy storage applications. The reasons include availability of double layer capacitors with high power densities (in both charge and discharge modes), and with energy densities approaching those of conventional rechargeable cells.

[0004] Double layer capacitors typically use as their energy storage element electrodes immersed in an electrolyte (an electrolytic solution). As such, a porous separator immersed in and impregnated with the electrolyte may ensure that the electrodes do not come in contact with each other, preventing electronic current flow directly between the electrodes. At the same time, the porous separator allows ionic currents to flow through the electrolyte

between the electrodes in both directions. As discussed below, double layers of charges are formed at the interfaces between the solid electrodes and the electrolyte.

[0005] When electric potential is applied between a pair of electrodes of a double layer capacitor, ions that exist within the electrolyte are attracted to the surfaces of the oppositely-charged electrodes, and migrate towards the electrodes. A layer of oppositely-charged ions is thus created and maintained near each electrode surface. Electrical energy is stored in the charge separation layers between these ionic layers and the charge layers of the corresponding electrode surfaces. In fact, the charge separation layers behave essentially as electrostatic capacitors. Electrostatic energy can also be stored in the double layer capacitors through orientation and alignment of molecules of the electrolytic solution under influence of the electric field induced by the potential. This mode of energy storage, however, is secondary.

[0006] In comparison to conventional capacitors, double layer capacitors have high capacitance in relation to their volume and weight. There are two main reasons for these volumetric and weight efficiencies. First, the charge separation layers are very narrow. Their widths are typically on the order of nanometers. Second, the electrodes can be made from a porous material, having very large effective surface area per unit volume. Because capacitance is directly proportional to the electrode area and inversely proportional to the widths of the charge separation layers, the combined effect of the large effective surface area and narrow charge separation layers is capacitance that is very high in comparison to that of conventional capacitors of similar size and weight. High capacitance of double layer capacitors allows the capacitors to receive, store, and release a large amount of electrical energy.

[0007] Electrical energy stored in a capacitor is determined using a well-known formula:

$$E = \frac{C*V^2}{2} \tag{1}$$

In this formula, E represents the stored energy, C stands for the capacitance, and V is the voltage of the charged capacitor. Thus, the maximum energy (E_m) that can be stored in a capacitor is given by the following expression:

$$C*V_r^2$$

$$E_m = \frac{}{2} \qquad , \qquad (2)$$

where V_r stands for the rated voltage of the capacitor. It follows that a capacitor's energy storage capability depends on both (1) its capacitance, and (2) its rated voltage. Increasing these two parameters may therefore be important to capacitor performance. Indeed, because the total energy storage capacity varies linearly with capacitance and as a second order of the voltage rating, increasing the voltage rating can be the more important of the two objectives.

[0008] Voltage ratings of double layer capacitors are generally limited by electrochemical reactions (e.g., reduction or oxidation) and breakdown that take place within the electrolytic solution in presence of an electric field induced between capacitor electrodes. Electrolytes currently used in double layer capacitors are of two kinds. The first kind includes aqueous electrolytic solutions, for example, potassium hydroxide and sulfuric acid solutions. Double layer capacitors may also be made with organic electrolytes, such as propylene carbonate (PC) solution, acetonitrile (AN) solution, liquid salts commonly referred to as ionic liquids, certain liquid crystal electrolytes, and even solid electrolytes.

[0009] Double layer capacitor cells manufactured using organic electrolytes and activated carbon have typically been rated at or below 2.3 volts in order to achieve a commercially acceptable number of charge-discharge cycles. Even small increases in the rated voltage above 2.3 volts tend to reduce substantially the number of charge-discharge cycles that the capacitors can withstand without significant deterioration in performance. As an approximation, every 100 millivolt increase in the rated capacitor voltage results in halving of the number of charge-discharge cycles that the capacitor can reliably withstand.

[0010] It would be desirable to decrease leakage current of double layer capacitors. It would also be desirable to improve reliability and durability of double layer capacitors, as measured by the number of charge-discharge cycles that a double layer capacitor can withstand without a significant deterioration in its operating characteristics. It would further be desirable to provide an electrode collector and/or ultracapacitor packaging that does not increase leakage current of the ultracapacitor. Additionally, it would be desirable to provide electrical devices, such as double layer capacitors, using such a collector and/or packaging.

[0011] A need thus exists for ultracapacitors that, have lower leakage currents compared to conventional ultracapacitors. A need also exists for methods and materials for making such ultracapacitors, and for electrical devices using such ultracapacitors or double layer capacitors.

SUMMARY

[0012] Various implementations hereof are directed to methods and electrical devices that may be directed to or may satisfy one or more of the above needs. An exemplar implementation herein disclosed is a method of making an electrical storage device with a reduced magnesium content in an aluminum alloy portion thereof.

[0013] In accordance with some aspects hereof, an electrode hereof may include a current collector having between about substantially no magnesium and less than about 0.7% magnesium. The current collector may be connected to electrode material to obtain an electrode for use in various electrical devices, including a double layer capacitor. The reduced magnesium aluminum of the current collector and/or packaging decreases current leakage of the capacitor.

[0014] These and other features and aspects of the present invention will be better understood with reference to the following description, drawings, and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Fig. 1, which includes sub-part Figs. 1A and 1B, illustrates, in a high-level fashion, a cross-section of an electrode assembly which may be used in a double layer capacitor;

[0016] Fig. 2 illustrates a cross-section of a jelly roll portion of a double layer capacitor;

[0017] Fig. 3 illustrates a cross-section of a double layer capacitor;

[0018] Fig. 4 illustrates data for corresponding double layer capacitors; and,

[0019] Fig. 5 illustrates selected operations of a process for incorporating a reduced magnesium aluminum component into the electrode assembly.

DETAILED DESCRIPTION

[0020] Reference will now be made in detail to one or more embodiments of the invention that are illustrated in the accompanying drawings. Same or similar reference numerals may be used in the drawings and the description to refer to the same or like parts. The drawings are in a simplified form and not to precise scale. For purposes of convenience and clarity only, directional terms, such as top, bottom, left, right, up, down, over, above, below, beneath, rear, and front may be used with respect to the accompanying drawings. These and similar directional terms should not be construed to limit the scope of the invention in any manner. In addition, the words couple, attach, connect, and similar expressions may be used interchangeably, unless the difference is noted or made otherwise clear from the context.

[0021] In this document, the words "implementation" and "variant" may be used to refer to a particular apparatus, process, or article of manufacture, and not necessarily always to one and the same apparatus, process, or article of manufacture. Thus, "one implementation" (or a similar expression) used in one place or context can refer to one particular apparatus, process, or article of manufacture; and, the same or a similar expression

in a different place can refer either to the same or to a different apparatus, process, or article of manufacture. Similarly, "some implementations," "certain implementations," or similar expressions used in one place or context may refer to one or more particular apparatuses, processes, or articles of manufacture; the same or similar expressions in a different place or context may refer to the same or a different apparatus, process, or article of manufacture. The expression "alternative implementation" and similar phrases are used to indicate one of a number of different possible implementations. The number of possible implementation is not necessarily limited to two or any other quantity. Characterization of an implementation as "an exemplar" or "exemplary" means that the implementation is used as an example. Such characterization does not necessarily mean that the implementation is a preferred implementation; the implementation may but need not be a currently preferred implementation.

[0022] The expression "ultracapacitor package" or "ultracapacitor packaging" and similar phrases signify the material that encases the other active element or elements, including the ultracapacitor and/or the ultracapacitor electrode or electrodes. Other phrases which may be used interchangeably include "housing"; "container" or "can." A "current collector," which is part of an electrode, may be discrete, or may be a part of or operably connected to or with the ultracapacitor package in many implementations.

[0023] The expression "active electrode material" and similar phrases signify material that is part of the electrode beyond simply providing a contact or reactive area approximately the size of the visible external surface of the electrode. The meaning of the word "film" is similar to the meaning of the words "layer" and "sheet"; and, these words do not necessarily imply a particular thickness or thinness of the material. When used in reference to an active electrode material film, the terms "powder," "particles," and the like refer to a plurality of small granules. References to "binder" are intended to include polymers, co-polymers, and similar ultra-high molecular weight substances capable of providing a binding of materials. Such substances are often employed as binder for promoting cohesion in loosely-assembled particulate materials, i.e., active filler materials that perform some useful function in a particular application.

[0024] Other and further definitions and clarifications of definitions may be found throughout this document. The definitions are intended to assist in understanding this

disclosure and the appended claims, but the scope and spirit of the invention should not be construed as strictly limited to the definitions, or to the particular examples described in this specification.

[0025]FIG.1, including sub-part Figs. 1A and 1B, illustrates, in a high level manner, respective cross-sectional views of an electrode assembly 100 which may be used in an ultracapacitor or a double layer capacitor. In Fig. 1A, the components of the assembly 100 are arranged as follows: a first current collector 105, a first active electrode film 110, a porous separator 120, a second active electrode film 130, and a second current collector 135. A first electrode 111 may include the first current collector 105 and the active electrode layer 110. Similarly, the second electrode 131 may include the second current collector 135 and the active electrode layer 130. An assembly or double-layer capacitor 100 may thus include two electrodes 111 and 131 kept apart by a porous separator 120. In some implementations, the first electrode may by convention be a positive electrode (anode) 111 and the second electrode a negative electrode (cathode) 131. In some implementations, a conductive adhesive layer (not shown) may be disposed on current collector 105 prior to bonding of the electrode film 110 (or likewise on collector 135 relative to film 130). In Fig. 1B, a double layer of films 110 and 110A are shown relative to collector 105, and a double layer 130, 130A relative to collector 135. In this way, a double-layer capacitor may be formed, i.e., with each current collector having a carbon film attached to both sides. A further porous separator 120A may then also be included, particularly for a jellyroll application, the porous separator 120A either attached to or otherwise disposed adjacent the top film 110A, as shown, or to or adjacent the bottom film 130A (not shown). The current collectors 105 and 135 may be made of the reduced magnesium aluminum material described herein, and by a process such as process 500 described in relation to Figure 5, below. An exemplary double layer capacitor using the electrode assembly 100 may further include an electrolyte and a container, for example, a sealed package or can, see FIG. 3, e.g., that holds the double layer capacitor structure of FIG. 1 and the electrolyte. The assembly 100 may thus be disposed within the container (can) and immersed in the electrolyte.

[0026] In many implementations, the current collectors 105 and 135 may be made from aluminum foil, the porous separator 120 may be made from one or more ceramics, paper, polymers, polymer fibers, glass fibers, and the electrolytic solution may include 1.5 M tetramethylammonium tetrafluroborate in organic solutions, such as PC or Acetronitrile

electrolyte (Other examples of electrolytic solutions, solvents and/or salts are described in much more detail below). The active electrode layers 110 and 130 can be made from activated carbon, optional conductive carbon, and binder particles. In one implementation the active electrode layers are manufactured without the use of solvents or additives. In one implementation, the active electrode layers are manufactured by a process that includes a dry mixing step, wherein dry binder particles, for example PTFE (though one or more of a variety of binder materials may be used), are dry mixed in a mill in a manner that binds dry activated carbon and optionally also dry conductive carbon particles in a porous matrix comprised of the three types of dry particles. The resulting dry process based product may subsequently be calendared one or more times to form a self-supporting active electrode film that may be used in the manufacture a double-layer capacitor product. Further detail is disclosed in co-pending and commonly assigned U.S. patent application, Ser. No. 10/817,701, filed 2 April 2004, which is incorporated herein by reference in its entirety for what it teaches and discloses.

[0027] When a voltage source is applied between the current collectors 105 and 135, an electric field may be created such that it spans the two layers. Note that the porous separator 120 may prevent electronic current flow between the electrodes 105 and 135. At the same time, the porous separator 120 may allow ionic current flow between these two electrodes. The electric field may thus drive the ions of the electrolytic solution towards the electrodes 105 and 135. Cations (positively charged ions) may be driven to what may here be referred to as the negative electrode 131, while anions (negatively charged ions) may be driven to the positive electrode 111. Double-layers of charges may be formed at the interfaces between the electrodes 111 and 131 and the electrolytic solution, with layers of oppositely-charged ions being created and maintained near the surface of each of these electrodes. Each set of the double-layer charges may in effect be a capacitor.

Referring now to FIG. 2, there is shown a view of active electrode layers of a double-layer capacitor. As shown, and as described relative to FIG. 1, top and bottom electrodes 111, 131 may be separated by a separator 120. In one implementation, separator 120 is a porous paper sheet of about 30 microns in thickness. In one implementation, the electrodes 111, 131 and separators 120 are subsequently rolled together in an offset manner, see FIGs. 1 and 3, about a central axis to form a configuration that is known to those skilled in the art as a "jellyroll" 200 and is illustrated in a top (or bottom) view by FIG. 2. In one implementation, wherein the electrodes are utilized in a double-layer capacitor product, the

storage capacitance may be between about 1 and about 5000 Farads. With appropriate changes and adjustments, other limits of capacitance will also be within the scope hereof.

[0029] Those skilled in the art will understand that offset exposed electrodes 111, 131 extend from the jellyroll, see FIG. 1, such that one collector extends from one end of the roll in one direction and another collector extends from an end of the roll in another direction. In one implementation, the collectors 105, 135 may be used to make electric contact with internal opposing ends of a sealed housing, see FIG. 3, which can include corresponding external terminals at each opposing end for completing an electrical contact. This is shown for example in FIG. 3, where there is illustrated a jellyroll 200 inserted into an open end of a housing. In one implementation, an insulator/seal 305 is placed along a top periphery of a housing 300 at an open end, and a cover 302 is placed on the insulator. During manufacture, the housing 300, insulator 305, and cover 302 may be mechanically curled together to form a tight fit around the periphery of the now sealed end of the housing, which after the curling process is electrically insulated from the cover by the insulator. When disposed in the housing 300, respective exposed collector extensions 135a of a jellyroll 200 make internal contact with the bottom end of the housing 300 and other extensions 105a make contact with the cover 302. In one implementation, external surfaces of the housing 300 or cover 302 may include or be coupled to standardized connections/connectors/terminals to facilitate electrical connection to the collectors of the jellyroll 200 within the housing 300. Contact between respective collector extensions 105a, 135a and the internal surfaces of the housing 300 and the cover 302 may be enhanced by welding, soldering, brazing, conductive adhesive, or the like. In one implementation, a welding process may be applied to the housing and cover by an externally applied laser welding process.

[0030] The current collector(s) may be metallic, and may be made for example from a continuous metal foil, metal mesh or nonwoven metal fabric. Typically, the current collector functions to provide a continuous electrically conductive substrate for the electrode film. The current collector may be pretreated prior to bonding to enhance its adhesion properties. Pretreatment of the current collector may include mechanical roughing, chemical pitting, and/or use of a surface activation treatment, such as corona discharge, active plasma, ultraviolet, laser, or high frequency treatment methods known to a person skilled in the art. In one implementation, the electrode films may be bonded to a current collector via an intermediate layer of conductive adhesive known to those skilled in the art.

[0031] In one implementation, the housing 300, cover 302, collectors 105, 135, and collector extensions 105a, 135a are of substantially the same metal, for example, aluminum. However, in many of the present implementations, even though aluminum alloys may be used for all such parts, different composite materials or different alloys may be chosen for particular parts in particular implementations. For a first example, the here referred to positive electrode collector 105 may be selected to be formed from a substantially pure aluminum, or an alloy of aluminum with a low magnesium content, or even an aluminum alloy, such as an Al 1100 (also known as commercially pure aluminum), which has a very low magnesium content, specified at substantially or about no magnesium (Al 1100 has according to at least one specification substantially no detectable magnesium, 0.1% Zn, 0.05-0.2 Cu and 0.95% Si and Fe). In some of these same implementations, the sometimes denominated negative electrode current collector 135 may be formed from an Al 6061, an aluminum alloy having from about 0.7% or about 0.8% to about 1.2% magnesium (Al 6061 is also by one specification includes 0.25% Zn, 0.15-0.4% Cu, 0.4-0.5% Cr and 0.4-0.8% Si and 0.7% Fe). In some of these implementations, further, it may be that the base packaging or can 300 may also be of Al 6061, and in some of these implementations, the cap 302 may be of a lower magnesium content, such as Al 1100. In other implementations, it may be that all or substantially all aluminum parts of an ultracapacitor device may be of a low magnesium alloy of aluminum.

It may be that the magnesium in the aluminum may and/or does leach out of the aluminum during use, particularly in electrical charging and discharging such that particularly at the positive electrode, the magnesium may be especially sensitive to being drawn out. This may be due to the oxidation reaction at the positive pole of the charging source, here the ultracapacitor. A metal such as magnesium may react more to an oxidation reaction. The negative pole, on the other hand involves a reduction reaction, in which the metal will not so easily react, i.e., will not reduce. Note, it may be understood that ultracapacitors may not necessarily have polarity as formed; i.e., it may be that either electrode 111 or 131 from the example of FIG. 1 might be useful as a positive electrode, and either could also/alternatively be the negative electrode. Similarly, the ultracapacitor packaging of FIG. 3 need not necessarily be of nor provide any polarity to the overall device. However, as one side or the other may or could operate as the positive pole, and the other as the negative, it may then be that material decisions could be used to impact the selection of

the positive and negative side. For example, in some cases, it may be decided to use a low magnesium aluminum such as Al1100 for all aluminum parts; however, as it is known that Al 1100 is a more expensive alloy of aluminum, and is much more soft (thus, not desirable for mechanical purposes), it may thus in one instance be preferable not to use Al 1100 for all aluminum parts of an ultracapacitor for both or either of cost and/or strength issues. Then, it may be decided to use Al 1100 for the positive collector 105 and Al6061 for the negative for strength and/or cost effectiveness of the jellyroll 200. Then, it may be decided further for either the entire package to formed from a stronger/lower cost aluminum such as Al6061, or it may be further desired to instead use Al1100 for the cap 302, but Al 6061 for the main body of the can 300. In this latter instance, or even if simply one pre-selected collector, e.g. collector 105, is formed of a low magnesium aluminum, then, it may be determined to pre-dispose the cap-side of the ultracapacitor as the positive side and the other side as the negative.

[0033] Once formed as shown in FIG. 3, then, an electrolyte can be added to the package through a filling/sealing port (not shown) to the sealed housing 300. In some implementations, the electrolyte is 1.5 M tetramethylammonium or tetrafluroborate in acetonitrile solvent. Other examples are set forth below. After impregnation and sealing, a finished energy storage product is thus made ready for commercial sale and/or subsequent use. Electrode products that include an active electrode film attached to a current collector and/or a porous separator may be used in a double layer capacitor and/or other electrical energy storage devices.

[0034]Following are several non-limiting examples of aqueous electrolytes which may be used in double-layer capacitors or ultracapacitors hereof: 1-molar Sodium sulphate, Na₂SO₄; 1-molar Sodium perchlorate, NaClO₄; 1-molar Potassium hydroxide, KOH; 1-molar Potassium chloride, KCl; 1-molar Perchloric acid, HClO₄; 1-molar Sulfuric acid, H₂SO₄; 1molar Magnesium chloride, MgCl₂; and, Mixed aqueous 1-molar MgCl₂/H₂O/Ethanol. Some non-limitative nonaqueous aprotic electrolyte solvents which can be used in capacitors include: Acetonitrile; Gamma-butyrolactone; Dimethoxyethane; N,N,-Dimethylformamide; Hexamethyl-phosphorotriamide; Propylene carbonate; Dimethyl carbonate; Tetrahydrofuran; 2-methyltetra-hydrofuran; Dimethyl sulfoxide; Dimethyl sulfite; Sulfolane methylenesulfone); Nitromethane; and, Dioxolane. Further, some non-limiting examples of electrolyte salts which can be used in the aprotic solvents include: Tetraalkylammonium salts

(such as: Tetraethylammonium tetrafluoroborate, (C₂H₅)₄NBF₄; Methyltriethylammonium tetrafluoroborate, (C₂H₅)₃CH₃NBF₄; Tetrabutylammonium tetrafluoroborate, (C₄H₉)₄NBF₄; and, Tetraethylammonium hexafluorophosphate (C₂H₅)NPF₆); Tetraalkylphosphonium salts (such as: Tetraethylphosphonium tetrafluoroborate (C₂H₅)₄PBF₄; Tetrapropylphosphonium tetrafluoroborate (C₃H₇)₄PBF₄; Tetrabutylphosphonium tetrafluoroborate (C₄H₉)₄PBF₄; Tetrahexylphosphonium tetrafluoroborate $(C_6H_{13})_4PBF_4;$ Tetraethylphosphonium hexafluorophosphate (C₂H₅)₄PPF₆; and, Tetraethylphosphonium trifluoromethylsulfonate (C₂H₅)₄PCF₃SO₃; and Lithium salts (such as: Lithium tetrafluoroborate LiBF₄; Lithium hexafluorophosphate LiPF₆; Lithium trifluoromethylsulfonate LiCF₃SO₃). Additionally, some Solvent free ionic liquids which may be used include: 1-ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl) imide EMIMBeTi; 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl imide EMIMIm; EMIBeti; EMIMethide; DMPIIm; DMPIBeti; DMPIMethide; BMIIm ; BMIBeti; BMIMethide; PMPIm; and, BMPIm. Examples for use as Anions include: bis(trifluoromethylsulfonyl)imide (CF₃SO₂)₂N⁻; bis(perfluoroethylsulfonyl)imide (C₂F₅SO₂)₂N⁻; and, tris(trifluoromethylsulfonyl)methide $(CF_3SO_2)_3C^-$ And, examples for use as Cations include: EMI: methylimidazolium; DMPI: 1,2-dimethyl-3-propylimidazolium; BMI: 1-butyl-3methylimidazolium; PMP: 1-N-propyl-3-methylpyridinium; and, BMP: 1-N-butyl-3methylpyridinium.

Referring now to FIG. 4, there are shown representative performance characteristics in chart 400 of double-layer capacitors manufactured in accordance with principles identified and used by the present method and device. Referring to FIG. 4, there is illustrated that a current collector comprising Al1100 as collector and package material made in accordance with principles disclosed herein may, at a 2.5 volt operating voltage, exhibit lower leakage current than that of a comparative capacitor comprising Al6061 as a collector and package material. Indeed, the actual test ultracapacitor of FIG. 4 included Al1100 as the collector material for both positive and negative collectors, and for the base portion of the package or can, see receptacle 300 of FIG. 3, with a cap 302 of Al6061. In one test where the Al6061 cap was in positive, the higher leakage current shown in FIG. 4 was produced; but, then, with the test ultracapacitor was flipped so that the Al6061 cap was in negative, and the can/receptacle of Al1100 was in positive, the lower leakage current shown in the graph of FIG. 4 was the result. Thus, as can be readily shown, a lower leakage current is demonstrated

with the low magnesium aluminum alloy in the positive side. A lower leakage current is indicative of a longer lasting power source, such as an ultracapacitor.

[0036] Now referring more particularly to drawing, FIG. 5, this illustrates selected operations of a process 500 for creating an electrode using a reduced magnesium aluminum alloy. Although the process operations are described substantially serially, operations may also be performed in alternative order, in conjunction or in parallel, in a pipelined manner, or otherwise. There is no particular requirement that the operations be performed in the same order in which this description lists them, except where explicitly so indicated, otherwise made clear from the context, or inherently required. Not all illustrated operations may be strictly necessary, while other optional operations may be added to the process 500.

In operation 505, a current collector with reduced or controlled magnesium content may be provided. This may be, for example a film or foil of Al1100. In operation 510, the reduced magnesium aluminum current collector may be attached to carbon electrode material. This would then form the electrode; often, typically the positive electrode, though this could also be used for the negative electrode as well. Though the process 500 ends here, further process operations could be implemented to then incorporate an electrode hereof therein. Exemplar such operations might include formation of a double-layer structure such as that shown in FIG. 1 including coupling with a porous separator and a further electrode, and even, in some instances, to a duplicate structure like that in FIG. 1. A further operation could then include forming a jelly roll like that in FIG. 2, and then alternatively also disposition of such a structure into a package not unlike that in FIG. 3.

[0038] Methods of use may then include, such as described above, use of electrodes and/or ultracapacitors hereof as energy storage or power supply devices, like for example, batteries, fuel cells, or the like. In such use, a circuit to receive power would be connected at one end to the positive (or effective positive) pole of an ultracapacitor hereof, and the other end of the circuit connected to the negative (or effective negative) pole hereof. Power may then be supplied to the circuit. Other uses will be readily developed and/or understood.

[0039] Although the particular systems and methods shown and described herein in detail are fully capable of attaining the above described object of this invention, it is understood that the description and drawings presented herein represent some, but not all,

implementations of the invention and are therefore representative of the subject matter which is broadly contemplated by the present invention. For example, although double-layer capacitors are discussed herein in the context of energy storage devices, those skilled in the art will identify that aspects and advantages described herein may apply to use in other energy storage devices, for example, batteries, fuel cells, and the like.

Therefore, this document describes in considerable detail the inventive methods for designing and fabricating electrodes and ultracapacitors of particular compositions and energy storage devices thereof. This has been done for illustrative purposes only. Neither the specific implementations of the invention as a whole, nor those of its features limit the general principles underlying the invention. In particular, the invention is not limited to the specific materials used in the illustrated implementations. The specific features described herein may be used in some implementations, but not in others, without departure from the spirit and scope of the invention as set forth. Many additional modifications are intended in the foregoing disclosure, and it will be appreciated by those of ordinary skill in the art that in some instances some features of the invention will be employed in the absence of a corresponding use of other features. The illustrative examples therefore do not define the metes and bounds of the invention and the legal protection afforded the invention, which function should be served by the claims presented herein and their equivalents.

CLAIMS

Accordingly, what is claimed is:

- 1. An electrode comprising:
 - a film of active electrode material; and
 - a current collector attached to the film of active electrode material, wherein the current collector has between about substantially no magnesium and less than about 0.7% magnesium by weight.
- 2. An electrode according to claim 1, wherein the current collector comprises aluminum.
- 3. An electrode according to claim 1, wherein the current collector comprises a substantially pure aluminum.
- 4. An electrode according to claim 1, wherein the current collector comprises an aluminum alloy.
- 5. An electrode according to claim 1, wherein the current collector comprises an aluminum alloy known as Al 1100.
- 6. An electrode according to claim 1, wherein the electrode is operably positive.
- 7. An electrode according to claim 1, wherein the collector of the electrode is operably connected to a positive contact.
- 8. An electrode according to claim 1, wherein the collector of the electrode is operably disposed within an electronic device package.
- 9. An electrode according to claim 1, wherein the collector of the electrode is operably disposed within an electronic device package connected to an electrical contact of the electronic device package.

10. An electrode according to claim 1, wherein the collector of the electrode is operably disposed within an electronic device package connected to a positive contact of the electronic device package.

- 11. An electrode according to claim 1, wherein the collector of the electrode is operably disposed within an electronic device package connected to an electrical contact of the electronic device package, and wherein the electrical contact is one or more of: a positive contact, aluminum, substantially pure aluminum, an aluminum alloy, and an aluminum alloy known as Al 1100.
- 12. An electrode according to claim 1, wherein the current collector is a first collector and the electrode is a first electrode which is operably disposed connected to a porous separator to which is connected a second electrode, the second electrode comprising:
 - a film of active electrode material; and
 - a second current collector attached to the film of active electrode material.
- 13. An electrode according to claim 12, wherein the second electrode is operably negative.
- 14. An electrode according to claim 12, wherein the second current collector of the second electrode comprises one or more of: substantially no magnesium, aluminum, substantially pure aluminum, an aluminum alloy, and an aluminum alloy known as Al 1100.
- 15. An electrode according to claim 12, wherein the second current collector of the second electrode comprises one or more of: an aluminum alloy, an aluminum alloy with a magnesium content of from about 0.7% to about 1.2% by weight, and an aluminum alloy known as Al 6061.
- 16. An electrode according to claim 12, wherein the first collector of the first electrode is operably disposed within an electronic device package connected to a first electrical contact of the electronic device package, and wherein the second collector of the second electrode is operably disposed within the electronic device package connected to a second electrical contact of the electronic device package.

17. An electrode according to claim 12, wherein the first collector of the first electrode is operably disposed within an electronic device package connected to a first electrical contact of the electronic device package, and wherein the second collector of the second electrode is operably disposed within the electronic device package connected to a second electrical contact of the electronic device package, and wherein the second contact is one or more of aluminum, substantially pure aluminum, an aluminum alloy, an aluminum alloy known as Al 1100, an aluminum alloy with a magnesium content of about 0.7% to about 1.2% by weight, and an aluminum alloy known as Al 6061.

18. An electrode according to claim 12, wherein the first collector of the first electrode is operably disposed within an electronic device package connected to a first electrical contact of the electronic device package, the first current collector of the first electrode comprising one or more of: substantially no magnesium, aluminum, substantially pure aluminum, an aluminum alloy, and an aluminum alloy known as Al 1100; and wherein the second collector of the second electrode is operably disposed within the electronic device package connected to a second electrical contact of the electronic device package, the second current collector of the second electrode comprising one or more of: an aluminum alloy, an aluminum alloy with a magnesium content of about 0.7% to about 1.2% by weight, and an aluminum alloy known as Al 6061.

19. An electrochemical double layer capacitor comprising:

a first electrode comprising a first current collector and a first film of active electrode material, the first film comprising a first surface and a second surface, the first current collector being attached to the first surface of the first film;

a second electrode comprising a second current collector and a second film of active electrode material, the second film comprising a third surface and a fourth surface, the second current collector being attached to the third surface of the second film;

a porous separator disposed between the second surface of the first film and the fourth surface of the second film;

a container;

an electrolyte;

wherein:

the first electrode, the second electrode, the porous separator, and the electrolyte are disposed in the container;

the first film is at least partially immersed in the electrolyte; the second film is at least partially immersed in the electrolyte;

the porous separator is at least partially immersed in the electrolyte;

each of the first and second films include aluminum, wherein the first current collector comprises one or more of: substantially no magnesium, aluminum, substantially pure aluminum, an aluminum alloy, and an aluminum alloy known as Al 1100, and wherein the second current collector comprises one or more of: an aluminum alloy, an aluminum alloy with a magnesium content of about 0.7% to about 1.2% by weight, and an aluminum alloy known as Al 6061.

20. A method of making an electrical device, the method comprising: providing a reduced magnesium aluminum alloy current collector; and, connecting the current collector to a carbon electrode material to form an electrode.

21. A method in accordance with claim 20, further comprising:

incorporating the electrode in reduced magnesium aluminum alloy packaging to form an ultracapacitor.

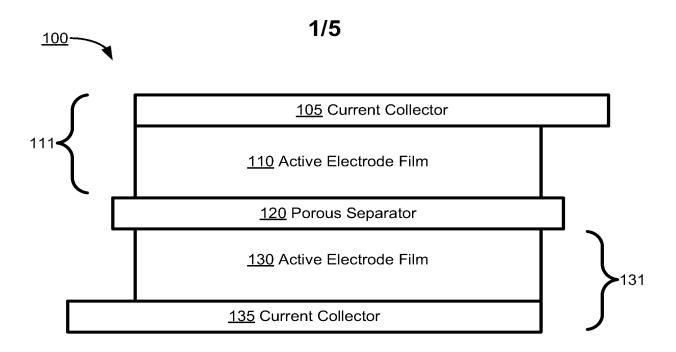
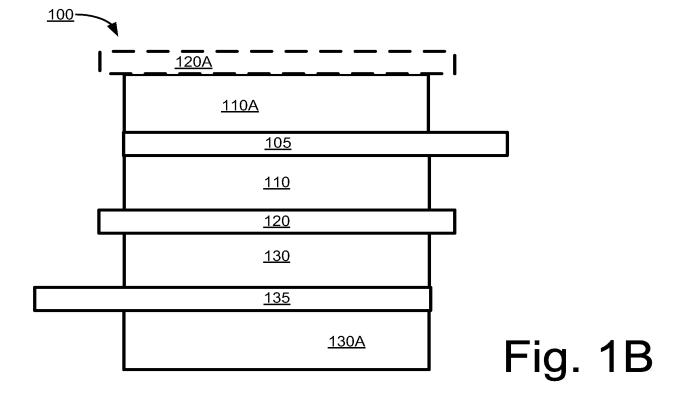
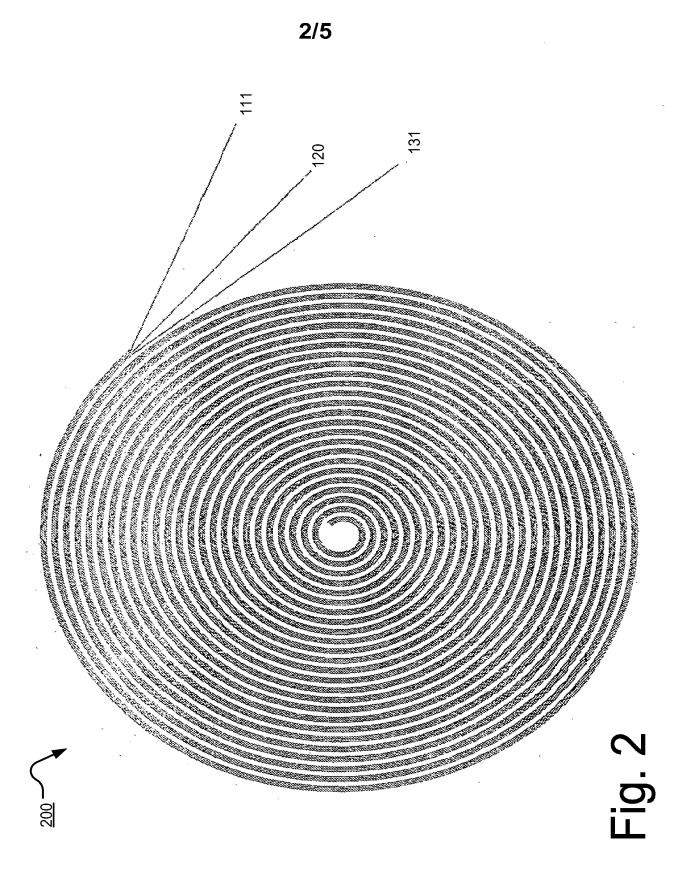


Fig. 1A







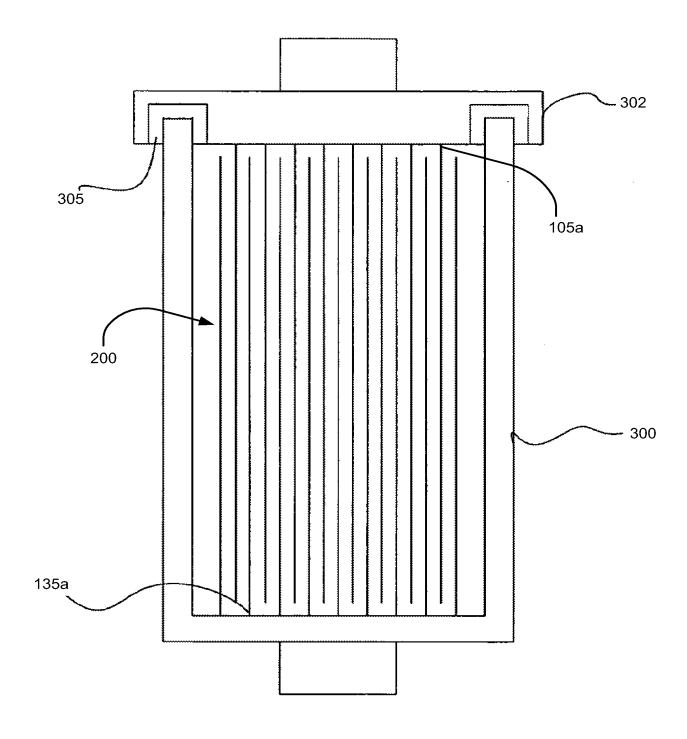


Fig. 3

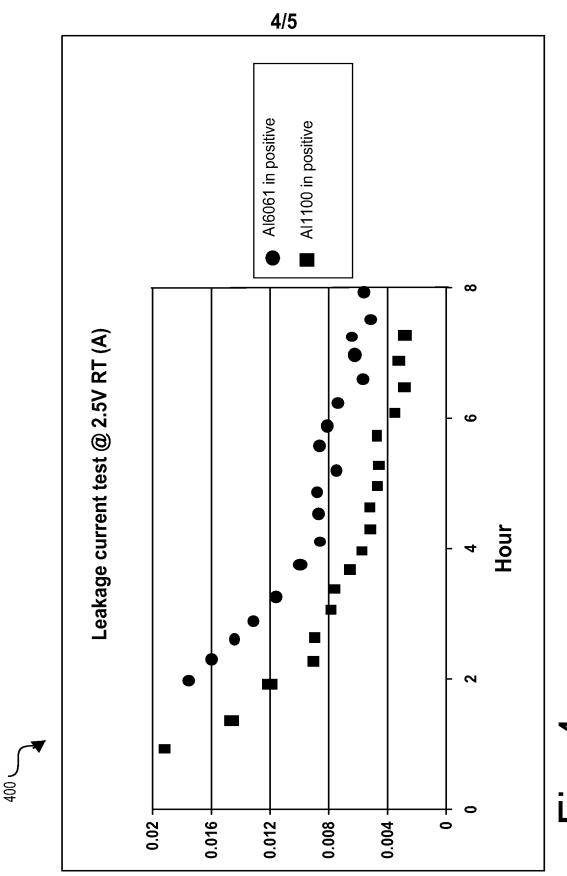


FIG. 4

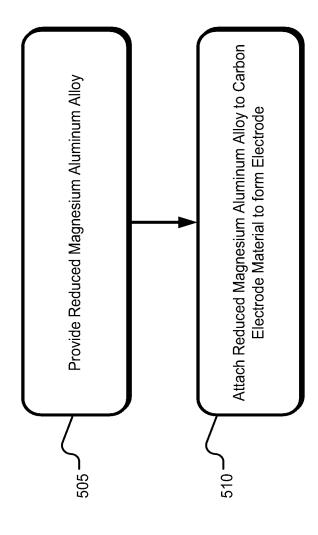


Fig. 5

International application No. PCT/US2008/055162

A. CLASSIFICATION OF SUBJECT MATTER

H01G 4/08(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8: H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility model since 1975. Japanese utility models and applications for utility model since 1975.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKIPASS(KIPO internal)

DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Х	US 5,518,823 A(TADAO FUJIHIRA et al.) 21 May 1996 See abstract and claim9.	1-18
Х	US 5,714,271 A(TOMOAKI YAMANOI et al.) 03 February 1998 See abstract and claims.	1-18
A	US 6,671,166 B1(JEAN-FRANCOIS PENNEAU et al.) 30 December 2003 See abstract and fig1.	1-18

	Further documents are listed in the continuation of Box C.	\boxtimes
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See patent family annex.

- Special categories of cited documents:
- document defining the general state of the art which is not considered to be of particular relevance
- earlier application or patent but published on or after the international filing date
- document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
- document referring to an oral disclosure, use, exhibition or other
- document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of mailing of the international search report

Date of the actual completion of the international search 29 JULY 2008 (29.07.2008)

29 JULY 2008 (29.07.2008)

Name and mailing address of the ISA/KR



Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seogu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140

KOH, JAE HYUN

Authorized officer

Telephone No. 82-42-481-5687



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2008/055162

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows: Group I, claims1~18 are directed to an electrode. Group II, claim19 is directed to an electorchemical double layer capacitor. Group III, claims20~21 are directed to a method of making an electrical device.
 As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-18
Remark on Protest The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee. The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation. No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/055162

CN 1063178 A 29.07 DE 69118131 CO 25.0 DE 69118131 T2 14.00 DE 691403774 A1 17.01 EP 0490574 B1 20.03 JP 04-213810 A 04.00 JP 04-213811 A 04.00 JP 04-213812 A 04.00 JP 3130054 B2 31.0 JP 3130056 B2 31.0 JP 3130056 B2 31.0 KR 10-9513775 B1 15.1 US 5165372 A 24.1 US 5714271 A 03.02.1998 CN 1039560 C 19.00 CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.00 EP 0662700 B1 01.10 JP 07-235457 A 05.00 JP 2907718 B2 21.00 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E 15.00 DE 69824160 C0 01.00 DE 69824160 T2 25.00 EP 0970496 B1 26.00 EP 09704	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 69118131 C0 25.00 DE 69118131 T2 14.00 DE 69118131 T2 14.00 EP 0490574 B1 20.00 JP 049213810 A 04.00 JP 04-213811 A 04.00 JP 04-213812 A 04.00 JP 3130055 B2 31.0 JP 3130056 B2 31.0 JP 3130056 B2 31.0 KR 10-9513775 B1 15.1 US 5165372 A 24.1 US 5714271 A 03.02.1998 CN 1039560 C 19.00 CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.00 EP 0662700 B1 01.10 JP 07-235457 A 05.00 JP 2907718 B2 21.00 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E 15.00 AU 1998-62982 A1 26.00 DE 69824160 C0 01.00 DE 69824160 T2 25.00 EP 0970496 A1 12.00 EP 0970496 B1 26.00 EP 0	US 5518823 A	21.05.1996		22.02.1995
DE 69118131 T2 14.00 EP 0490574 A1 17.00 EP 0490574 B1 20.00 JP 04-213810 A 04.00 JP 04-213811 A 04.00 JP 04-213812 A 04.00 JP 3130055 B2 31.0 JP 3130056 B2 31.0 JP 3130056 B2 31.0 KR 10-9513775 B1 15.1 US 5165372 A 24.1 US 5714271 A 03.02.1998 CN 1039560 C 19.00 CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.00 EP 0662700 A1 12.00 EP 0662700 B1 01.10 JP 07-235457 A 05.00 JP 2907718 B2 21.00 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E 15.00 AU 1998-62982 A1 26.00 DE 69824160 C0 01.00 DE 69824160 T2 25.00 EP 0970496 A1 12.0 EP 0970496 B1 26.00 EP 0970496 B1 27.00 EP 0970				29.07.1992 25.04.1996
EP 0490574 A1 17.00 EP 0490574 B1 20.03 JP 04-213810 A 04.04 JP 04-213811 A 04.03 JP 04-213812 A 04.04 JP 3130054 B2 31.0 JP 3130056 B2 31.0 JP 31				14.08.1996
EP 0490574 B1 20.00 JP 04-213810 A 04.06 JP 04-213811 A 04.06 JP 04-213812 A 04.06 JP 3130054 B2 31.0 JP 3130056 B2 31.0 JP 3130056 B2 31.0 KR 10-9513775 B1 15.1 US 5165372 A 24.1 US 5714271 A 03.02.1998 CN 1039560 C 19.06 CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.07 EP 0662700 B1 01.16 JP 07-235457 A 05.06 JP 2907718 B2 21.06 KR 10-1995-0020801 A 24.07 US 6671166 B1 30.12.2003 AT 268052 E 15.06 AU 1998-62982 A1 26.06 DE 69824160 C0 01.07 DE 69824160 C0 01.07 DE 69824160 C0 01.07 DE 69824160 C0 01.07 DE 69924160 T2 25.06 EP 0970496 B1 26.06 EP 0970496 B1 26.07 EP 0970496 B1 26.07 EP 0970496 B1 26.07 EP 0970496 B1 26.07 EP 2759211 A1 07.07				17.06.1992
US 5714271 A 03.02.1998 ON 1039560 C ON 1112721 A ON 100 B ON				20,03,1996
US 6671166 B1 US 6671166 B1 US 6671166 B1 US 66701466 B1 US 6670046 B1 US 66700466 B1 US			JP 04-213810 A	04.08.1992
US 6671166 B1 US 6671166 B1 US 6671166 B1 US 670496 B1 US 670496 B1 US 7130055 B2 31.0 UP 3130056 B2 31.0 UR 10-9513775 B1 15.1 US 5165372 A 24.1 US 5714271 A 03.02.1998 CN 1039560 C 19.00 CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.00 EP 0662700 B1 01.10 JP 07-235457 A 05.00 JP 2907718 B2 21.00 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E 15.00 DE 69824160 C0 DE 69824160 T2 25.00 EP 0970496 A1 12.0 EP 0970496 B1 26.00 FR 2759211 A1 07.00 FR 2759211 A1 07.00				04.08.1992
US 5714271 A 03.02.1998 CN 1039560 C CN 1112721 A CN 1112721 A CN 1112721 A CN 1112721 A CP 0662700 A1 CP 0662700 B1 CP 0662700 B1 CR 10-1995-0020801 A CR 10-1995-0020801 A CR 11-2003 AT 268052 E CR 25.00 CR 25.00 CR 1166 B1 CR 10-1995-0020801 A CR 268052 E CR 10-1995-0020801 A CR 268052 E CR 2759211 A1 CR 2759211 A1 CR 2759211 A1 CR 2759211 B1				04.08.1992
US 5714271 A 03.02.1998 CN 1039560 C CN 1112721 A CN 1112721 A CN 10405971 CO CN 1112721 A CN 1069405971 CO CN 1112721 A CN 1069405971 T2 CN 10662700 A1 CN 107-235457 A CN				31.01.2001
US 5714271 A 03.02.1998 CN 1039560 C CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.00 EP 0662700 B1 JP 07-235457 A 05.00 JP 2907718 B2 21.00 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E AU 1998-62982 A1 DE 69824160 C0 DE 69824160 T2 25.00 EP 0970496 B1 12.00 EP 0970496 B1 26.00 EP 0970496 B1				31.01.2001 31.01.2001
US 5165372 A 24.1 US 5714271 A 03.02.1998 CN 1039560 C 19.08 CN 1112721 A 29.1 DE 69405971 C0 06.1 DE 69405971 T2 22.0 EP 0662700 A1 12.00 EP 0662700 B1 01.10 JP 07-235457 A 05.08 JP 2907718 B2 21.08 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E 15.08 AU 1998-62982 A1 26.08 DE 69824160 C0 01.07 DE 69824160 T2 25.08 EP 0970496 B1 12.0 EP 0970496 B1 26.08 EP 2759211 A1 07.08 EP 2759211 B1 30.08				15.11.1995
US 6671166 B1 30. 12.2003 AT 268052 E AU 1998-62982 A1 DE 69824160 T2 EP 0970496 B1 12.00 EP 0970496 B1 EP 0970486 ER 2759211 B1 CN 1112721 A 29. 1 DE 69405971 C0 06. 1 DE 69405971 T2 22. 0 EP 0662700 A1 12. 0 EP 0662700 B1 01. 10 JP 07-235457 A 05. 05 JP 2907718 B2 21. 06 KR 10-1995-0020801 A 24. 07 EP 0970496 B1 EP 0970496 B1 EP 0970496 B1 ER 2759211 B1 30. 06				24. 11. 1992
US 6671166 B1 30.12.2003 AT 268052 E AU 1998-62982 A1 DE 69824160 C0 DE 69824160 T2 EP 0970496 B1 DE 69805971 T2 DE 0662700 B1 DE 06	 US 5714271 A	03.02.1998		19.08.1998
US 6671166 B1 30.12.2003 AT 268052 E AU 1998-62982 A1 DE 69824160 C0 DE 69824160 T2 EP 0970496 A1 12.07 EP 0662700 B1 D1.10 D2 69824161 C0 D3 0970496 B1 EP 0970496 B1 D4 07-235457 A D5 08 D6 09824161 C0 D7 0970496 B1 D8 0970496 B1 D8 0970496 B1 D8 07 08 07 08 08 D8 0970496 B1 D8 07 08 08 D8 0970496 B1 D8 07 08 08 D8 0970496 B1 D8 07 08 D8 0970496 B1				29.11.1995
EP 0662700 A1 12.00 EP 0662700 B1 01.10 JP 07-235457 A 05.00 JP 2907718 B2 21.00 KR 10-1995-0020801 A 24.00 US 6671166 B1 30.12.2003 AT 268052 E 15.00 AU 1998-62982 A1 26.00 DE 69824160 C0 01.00 DE 69824160 T2 25.00 EP 0970496 A1 12.0 EP 0970496 B1 26.00 FR 2759211 A1 07.00 FR 2759211 B1 30.00				06.11.1997
US 6671166 B1 30.12.2003 AT 268052 E AU 1998-62982 A1 DE 69824160 C0 DE 69824160 T2 EP 0970496 A1 12.0 EP 0970496 B1 26.00 EP 0970496 B1 26.00 EP 0970496 B1 26.00 EP 0970496 B1 EP 070496 B1 EP 070496 B1 ER 2759211 A1 OF 08				22.01.1998 12.07.1995
US 6671166 B1 30.12.2003 AT 268052 E 15.06 AU 1998-62982 A1 26.06 DE 69824160 C0 01.07 DE 69824160 T2 25.06 EP 0970496 A1 12.0 EP 0970496 B1 26.06 FR 2759211 A1 07.06 FR 2759211 B1 30.06				01.10.1997
US 6671166 B1 30.12.2003 AT 268052 E AU 1998-62982 A1 DE 69824160 C0 DE 69824160 T2 EP 0970496 A1 EP 0970496 B1 EP 0970496 B1 ER 2759211 A1 OT. 08 FR 2759211 B1 30.10.00				05.09.1995
US 6671166 B1 30.12.2003 AT 268052 E 15.06 AU 1998-62982 A1 26.06 DE 69824160 C0 01.07 DE 69824160 T2 25.06 EP 0970496 A1 12.0 EP 0970496 B1 26.06 FR 2759211 A1 07.06 FR 2759211 B1 30.06				21.06.1999
AU 1998-62982 A1 26.08 DE 69824160 C0 01.03 DE 69824160 T2 25.08 EP 0970496 A1 12.0 EP 0970496 B1 26.08 FR 2759211 A1 07.08 FR 2759211 B1 30.09			KR 10-1995-0020801 A	24.07.1995
DE 69824160 C0 01.07 DE 69824160 T2 25.09 EP 0970496 A1 12.0 EP 0970496 B1 26.09 FR 2759211 A1 07.08 FR 2759211 B1 30.09	US 6671166 B1	30.12.2003		15.06.2004
DE 69824160 T2 25.09 EP 0970496 A1 12.0 EP 0970496 B1 26.09 FR 2759211 A1 07.09 FR 2759211 B1 30.09				26.08.1998
EP 0970496 A1 12.0 EP 0970496 B1 26.09 FR 2759211 A1 07.08 FR 2759211 B1 30.04				01.07.2004 25.05.2005
EP 0970496 B1 26.09 FR 2759211 A1 07.09 FR 2759211 B1 30.04				12.01.2000
FR 2759211 A1 07.08 FR 2759211 B1 30.04				26.05.2004
				07.08.1998
WO OO 25260 A1 12 O				30.04.1999
75. 01 1A 80000-08 UW			WO 98-35369 A1 	13.08.1998